

# PATENT SPECIFICATION

(11) 1267287

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NO DRAWINGS

(21) Application No. 42563/70 (22) Filed 4 Sept. 1970  
 (31) Convention Application No. 69945 (32) Filed 5 Sept. 1969 in  
 (33) Japan (JA)  
 (45) Complete Specification published 15 March 1972  
 (51) International Classification G 03 c 1/06  
 (52) Index at acceptance  
 G2C A2 AX C7 C8BX C9H3B3B C9H3B3E C9H3B4B  
 C9H3B4X



## (54) COLOUR PHOTOGRAPHIC MATERIALS

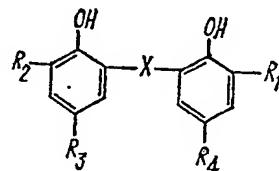
(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese Body Corporate of 1—10 3-Chome, Nihonbashi-Muro-Machi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a color photograph bearing a color image comprising an azomethine or indoaniline dye together with a phenol derivative as a fading-preventing agent.

It is well known that a color photograph is obtained by subjecting a light-sensitive silver halide color photographic material to color development according to the oxidation condensation reaction of a primary aromatic amino compound with a coupler, thereby forming a color image comprising an azomethine, indoaniline, or indophenol dye. In this case, subtractive color photography is employed for reproduction of the color image, and cyan, magenta and yellow dyes are formed by the color development, in general. Ordinarily, the cyan dye is formed from a phenol or naphthol type coupler, the magenta dye from a pyrazolone type coupler, and the yellow dye from an acylacetamide type coupler. These couplers are added to developers or have previously been incorporated into silver halide photographic emulsions.

However, it is also well known that a color image formed according to such a color development process as mentioned above does not have satisfactory light-fastness, chiefly to ultraviolet rays or visible light, but fades with relative ease when irradiated with ultraviolet rays or visible light. In order to overcome this drawback, there have heretofore been studied many processes for improving the light fastness of color images by incorporating an ultraviolet ray-absorbing agent in a light-sensitive silver halide color photographic material, thereby decreasing the dose of ultraviolet rays to which the resulting color image is subjected. However, in order to impart satisfactory light fastness to a color image by use of an ultraviolet ray-absorbing agent, a large amount of said agent is required, and the color image thereby becomes stained due to the coloration effected by the ultraviolet ray-absorbing agent itself. Further, the use of an ultraviolet ray-absorbing agent is not at all effective for prevention of the fading of a color image due to visible light, and thus the improvement in light fastness of color image by use of an ultraviolet ray-absorbing agent is limited.

In view of this state of affairs, we have made studies for years in order to improve the light-fastness of color images formed by color development of light-sensitive silver halide color photographic materials. As the result, it has been found that the light fastness of a developed color image present in a color photograph is greatly improved by making present, together with a dye in the developed color image, a bisphenol derivative of the general formula,



wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently represents a straight chain or branched chain aliphatic hydrocarbon radical having 1 to 18 carbon atoms, the total sum of carbon atoms of said R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> being less than 32; and X is —S—, —O—, —SO<sub>2</sub>— or

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where n is 0 or an integer of 1 to 3; and R<sub>5</sub> represents a hydrogen atom or a lower alkyl group (namely an alkyl group having 1—4 carbon atoms).

The above-mentioned fading-reducing agent employed in the present invention is used for the improvement in light fastness of cyan, magenta and yellow color images formed by color development. Cyan, magenta and yellow couplers to be used for the formation of these color images are not limited, and may be any of such types which are alkali-soluble and alkali solutions thereof are incorporated into silver halide photographic emulsions, and which are soluble in a high boiling organic solvent to give a solution which can be dispersed in an aqueous gelatine solution or added to silver halide photographic emulsions.

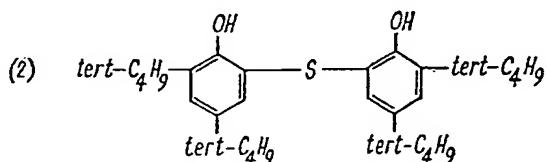
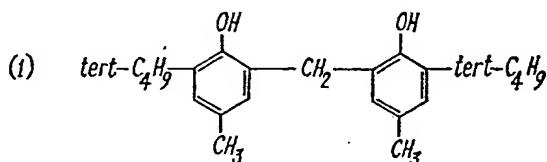
The fading-reducing agent employed in the present invention may be incorporated into any or all of the layers of a light-sensitive silver halide photographic material, i.e. photographic emulsion layers in which cyan, magenta and yellow dyes will be formed by color development. Further, when applied to a transfer diffusion method, the fading-reducing agent may be incorporated not only into such photographic emulsion layers as mentioned above but also into receptive layers. That is, it is sufficient that the fading-preventing agent is present together with any or all of dyes forming the color image of a finally obtained photograph, e.g. in a photographic negative.

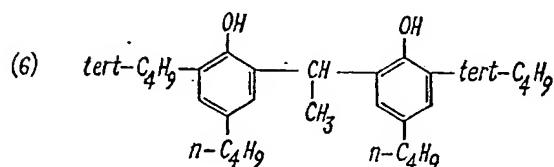
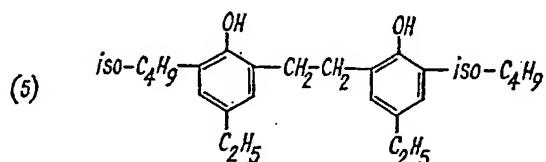
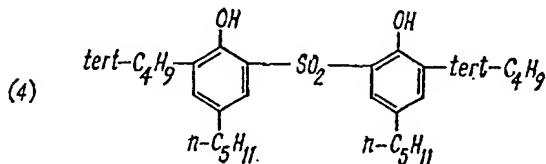
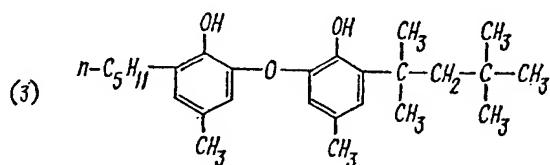
The fading-reducing agent used in the present invention is hardly water-soluble, but is soluble in a low boiling organic solvent such as methyl acetate, ethyl acetate, carbon tetrachloride, chloroform, methanol, ethanol, n-butanol, dioxane, acetone, benzene, dimethylformamide or dimethyl sulfoxide, a high boiling solvent such as tricresyl phosphate, di-n-butyl phthalate or ethyl N,N-diphenyl carbamate, or a mixed solvent comprising said low and high boiling solvents. The resulting solution is charged into a protective colloid solution, dispersed by means of a colloid mill or a homogenizer and then added to, for example, a silver halide photographic emulsion containing a coupler. Depending on the type of the coupler, the fading-reducing agent and the coupler may be dissolved in an organic solvent and then added to an aqueous gelatine solution.

Examples of the fading-reducing agent used in the present invention are as shown below, but these are, of course, not limitative. Most conveniently the radicals, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> have not more than 8 carbon atoms each. Each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently may be, for example, methyl, ethyl, n-butyl, isobutyl, t-butyl, n-amyl, or 2,4,4-trimethyl-2-pentyl.

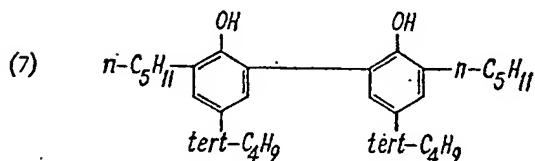
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The amount of the fading-reducing agent to be added varies depending on the kind of said agent and the coupler employed and on the kind of layer to which the agent is applied, but is usually within the range from 1 to 100% by weight based on the weight of the coupler. A silver halide photographic emulsion containing the fading-reducing agent and a coupler is coated on a support such as baryta paper or film base to form a photographic emulsion layer. Into this photographic emulsion layer, or a lower or upper layer thereof, may be incorporated an ultraviolet ray-absorbing agent. Thus the fading-reducing agent of the present invention can be used in combination with the ultraviolet ray-absorbing agent, whereby the light fastness of the resulting color image can be enhanced. Examples of the ultraviolet ray-absorbing agent to be used in the above case are benzophenone, acrylonitrile, thiazolidone, benzotriazole, stilbene, oxazole, thiazole and imidazole type compounds, though these are, of course, not limitative.

When, as mentioned above, dyes forming the color image of a color photograph are present together with a fading-reducing agent represented by the aforesaid general formula, the resulting developed color image is markedly improved in fastness to ultraviolet rays and visible light, as will be clear from the examples set forth later. Further, all the fading-reducing agents used in the present invention are substantially colorless and hence do not stain the resulting color images.

The incorporation of the fading-reducing agent does not bring about any injurious effect in the color development, and even when it is present together with a

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dye formed by color development, no change in hue is observed. Moreover, the fading-reducing agent has no detrimental interactions with commonly used photographic additives.

The present invention is illustrated below with reference to Examples.

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#### EXAMPLE 1

2 g. of the exemplified compound (4) was dissolved in a mixed solution of 1 g. of tricresyl phosphate and 4 g. of ethyl acetate. The resulting solution was added to 40 cc. of a 5% aqueous gelatine solution containing saponin and then dispersed by means of a homogenizer. The whole amount of the resulting dispersion was added to 400 cc. of a silver chlorobromide emulsion containing 10 g. of sodium 1-hydroxy-N-octadecyl-2-naphthamide-4-sulfonate (coupler). Thereafter, the emulsion was coated on a baryta paper and then dried to prepare a sample of the present invention.

For comparison, a control sample was prepared in the same manner as above, except that the compound (4) was not used.

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The sample of the present invention and the control sample were individually exposed to white light, subjected to color development, stopping, fixing, bleaching, water-washing and drying, and exposed for 5, 10 and 20 hours by means of a Xenon fade meter to calculate the percentage ( $D/D_0 \times 100$ ) of the density after exposure ( $D$ ) to the density before exposure ( $D_0$ ). The results were as shown in Table 1.

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TABLE 1

	Sample	D/D <sub>0</sub> × 100		
		5	10	20
	Control sample	82	65	41
20	Sample of the present invention	94	88	76
	Exposure time (hrs.)	5	10	20

( $D_0 = 1.0$ )

As is clear from the results shown in Table 1, the light fastness of the sample of the present invention is greatly improved.

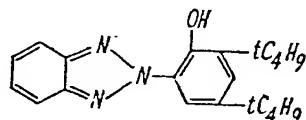
#### EXAMPLE 2

25 A mixture comprising 8.0 g. of the cyan coupler 2-(p-tert-amylphenoxy-p-benzoyl)-amino-4-chloro-5-methylphenol, 3.0 g. of the exemplified compound (2) and 3.0 g. of the ultraviolet ray-absorbing agent 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-benzotriazole having the formula:

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was dissolved in a mixed solution of 8 g. of tricresyl phosphate and 20 g. of ethyl acetate. The resulting solution was added to 200 cc. of a 5% aqueous gelatine solution containing saponin and then dispersed by means of a homogenizer. Subsequently, the resulting dispersion was added to 400 cc. of a red-sensitive silver iodobromide emulsion, which was then coated on a film base, followed by drying, to prepare a sample (I) of the present invention.

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Further, a control sample, a sample (II), and a sample (III) were prepared in the same manner as above, except that the control sample contained neither the exemplified compound (2) nor the ultraviolet ray-absorbing agent, sample (II) did not contain the exemplified compound (2), and sample (III) did not contain the ultraviolet ray-absorbing agent.

The samples (I) to (III) and the control sample were individually exposed to white light, subjected to color development, stopping, fixing, bleaching washing and drying, and then exposed for 10, 20 and 40 hours by means of a Xenon fade meter to measure the density variation of the samples in the same manner as in Example 1. The results were as shown in Table 2.

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TABLE 2

Sample	D/Do × 100		
Control sample	85	71	54
Sample (I)	100	98	95
Sample (II)	94	87	80
Sample (III)	97	92	90
Exposure time (hrs.)	10	20	40

(Do = 1.0)

From the results of Table 2, it is evident that the samples (I) and (III) of the present invention show excellent light fastness, which for Sample (I) is further enhanced by use of the exemplified compound (2) in combination with the ultraviolet ray-absorbing agent.

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## EXAMPLE 3

A mixture comprising 10 g. of the magenta coupler 1-(2,4-dimethyl-6-chlorophenyl)-3-{3-[ $\alpha$ -(3-pentadecylphenoxy)butyramido]benzamido}-5-pyrazolone and 4 g. of the exemplified compound (1) was dissolved in a mixed solution of 5 g. of dibutyl phthalate and 20 g. of ethyl acetate. The resulting solution was added to 200 cc. of a 5% aqueous gelatine solution containing saponin and then dispersed by means of a homogenizer. Subsequently, the dispersion was added to 350 cc. of a green-sensitized silver chlorobromide emulsion, which was then coated on a baryta paper.

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On the other hand, 7 g. of the same ultraviolet ray-absorbing agent as in Example 2 was dissolved in a solution of 10 g. of tricresyl phosphate in 20 g. of ethyl acetate. The resulting solution was added to 300 cc. of a 10% aqueous gelatine solution containing saponin and then dispersed by means of a homogenizer. The thus obtained dispersion was coated on the aforesaid silver chlorobromide emulsion layer so that the amount of the ultraviolet ray-absorbing agent became 7 mg. per 100 cm<sup>2</sup>, followed by drying, to prepare a sample (I).

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Further, samples (II) and (III) and a control sample were prepared in the same manner as above, except that sample (II) did not contain the ultraviolet ray-absorbing agent. Sample (III) did not contain the exemplified compound (1), and the control sample contained neither the ultraviolet ray-absorbing agent nor the exemplified compound (1).

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The thus prepared samples (I) to (III) and the control sample were individually subjected to the same photographic treatments as in Example 1, and then exposed for 5, 10 and 20 hours by means of a Xenon fade meter to calculate the density variation of the samples in the same manner as in Example 1. The results were as shown in Table 3.

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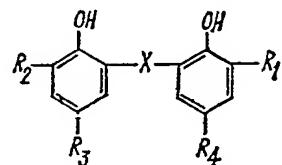
TABLE 3

Sample	D/Do × 100		
Control sample	70	53	38
Sample (I)	100	100	96
Sample (II)	98	96	87
Sample (III)	83	66	50
Exposure time (hrs.)	5	10	20

From the results of Table 3, it is clear that the samples (I) and (II) of the present invention have excellent light fastness.

WHAT WE CLAIM IS:—

5 1. A colour photograph which contains, as an agent for reducing the fading of colour, a compound of the general formula,



10 wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> independently represents a straight or branched chain aliphatic hydrocarbon radical having 1 to 18 carbon atoms, the total sum of the carbon atoms in the radicals R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> being less than 32; and —X— represents —S—, —O—, —SO<sub>2</sub>—, a single bond connecting the two benzene rings shown, or a radical of formula



15 n being 1, 2 or 3, and R<sub>5</sub> representing a hydrogen atom or an alkyl radical having 1—4 carbon atoms.

15 2. A colour photograph according to claim 1, which also contains an ultraviolet ray-absorbing agent.

3. A colour photograph according to claim 1 or 2 in the form of a negative.

20 4. A colour photograph according to any one of claims 1—3, in which the agent for reducing the fading of colour is of the formula given in claim 1 wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> independently represents a straight or branched chain aliphatic hydrocarbon radical having 1 to 8 carbon atoms.

5. A colour photograph according to any preceding claim wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> represents straight or branched chain alkyl radicals.

25 6. A colour photograph according to claim 5 wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently represents a methyl, ethyl, n-butyl, iso-butyl, t-butyl, n-amyl or 2,4,4-trimethyl-2-pentyl radical.

7. A colour photograph according to any preceding claim wherein R<sub>1</sub> is the same as R<sub>2</sub> and/or wherein R<sub>3</sub> is the same as R<sub>4</sub>.

30 8. A colour photograph according to any preceding claim wherein —X— represents —CH<sub>2</sub>—, —CH<sub>2</sub>CH<sub>2</sub>— or —CH—



9. A colour photograph according to claim 1 wherein the agent for reducing the fading of colour is one or more of compounds (1) to (7) specifically hereinbefore set out.

10. A light-sensitive photographic silver halide emulsion which contains a colour coupler and an anti-fade agent as specified in any one of claims 1 and 4—9.

11. An emulsion according to claim 10 wherein the colour coupler is a cyan, magenta or yellow colour coupler.

5 12. An emulsion according to claim 10 or 11 wherein the anti-fade agent is present in an amount of 1—100% by weight of the colour coupler.

13. A light-sensitive colour photographic film which comprises at least one layer of an emulsion claimed in claim 10, 11 or 12 carried on a support.

14. A colour photograph, silver halide colour emulsion or colour photographic film containing an anti-fade agent, which agent comprises one or more compounds having two 2,4-disubstituted phenol nucleii linked together through their 6-positions, substantially as herein described.

10 15. A colour photograph according to any one of claims 1—9, emulsion according to any one of claims 10—12 or film according to claim 13, substantially as described in any one of the Examples.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

